(19) **United States**

(12) **Patent Application Publication** (10) Pub. No.: **US 2008/0311434 A1**
Rey-Mermet et al. (43) **Pub. Date: Dec. 18, 2008**

(54) **METALLIC SUPPORTING GRID FOR THIN ELECTROLYTE MEMBRANE IN SOLID OXIDE FUEL CELLS**

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Publication Classification

(57) **ABSTRACT**

A solid oxide fuel cell structure obtainable by selective electro-chemical processing, comprising an electrolyte membrane (4) formed by a thin film more than 50 nm but less than 10 μm thick, covering a supporting structure (1) made of a bulk substrate, the supporting structure having at least one 100 μm to 100 mm wide opening that is covered by the electrolyte membrane (4). A metallic grid (9) is applied over the electrolyte membrane (4) and serves at the same time as structural element to support the membrane and as current collector. The metallic grid (9) has gridlines that are higher than the membrane thickness and whose height to width ratio is larger than 0.5, and a mesh size about 10 to 1000 times smaller than the width of said opening. The metallic grid (9) can be applied on top of a patterned metallic sub-layer structure (7,7*a*) arranged for supplying a fine distribution of current and increasing the density of electrolyte-electrode boundaries exposed to the fluid. The structure is useful for current generation and as a gas sensor.
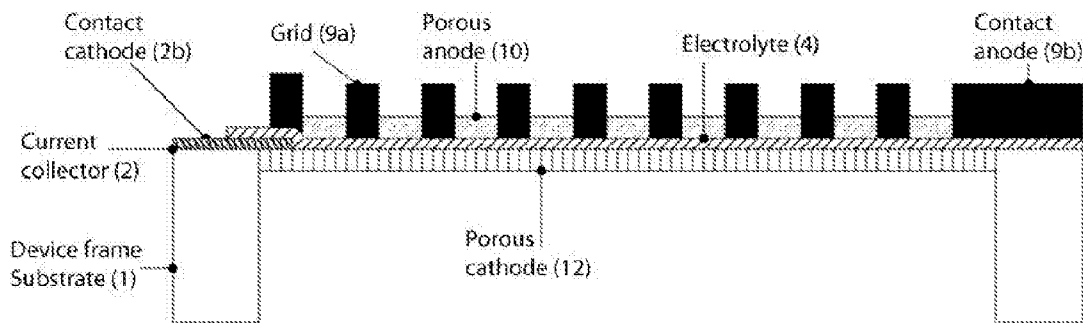
Figure 1-1

Figure 1-2

Figure 2-1

Figure 2-2

Figure 2-3

Figure 2-4

5

4

2

1

Figure 2-5

2b

L2

4

2

1

Figure 2-6

6

4

2

1

Figure 2-7

7

t3

4

6

2

1

Figure 2-8

L3   w3   w4   7 4 2 L4

1

Figure 2-9

4 7 8 2

1

Figure 2-10
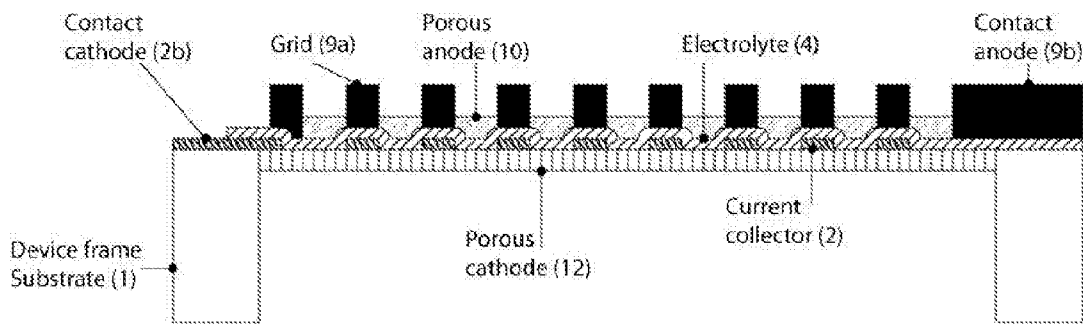
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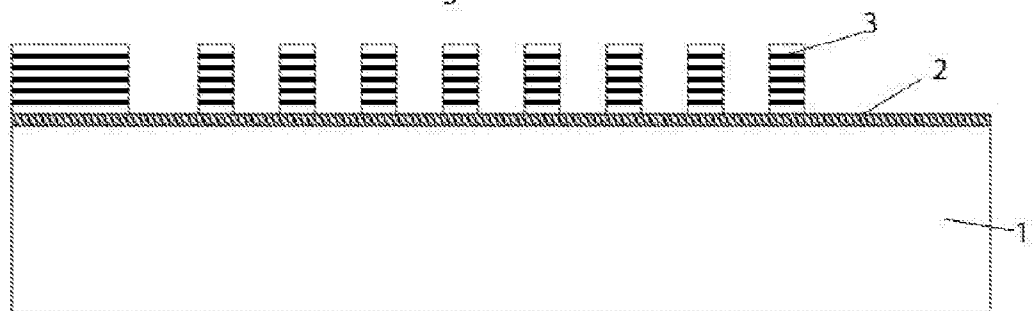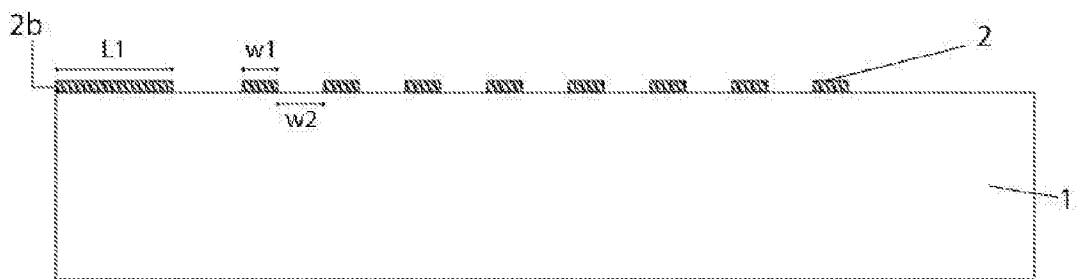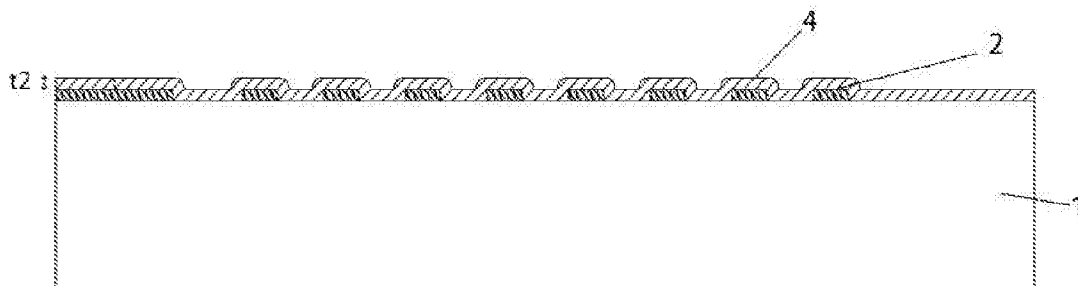
Figure 2-11

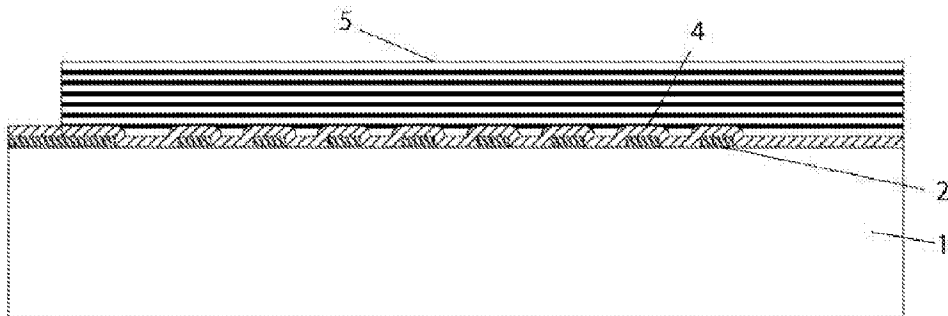t4 w5 w6 9a 9b 7 4 2 1
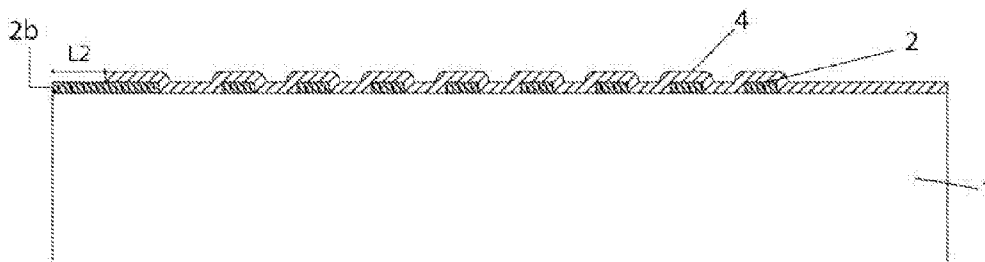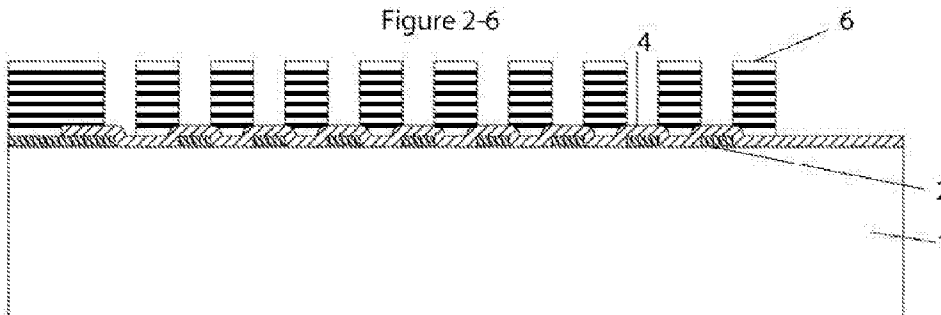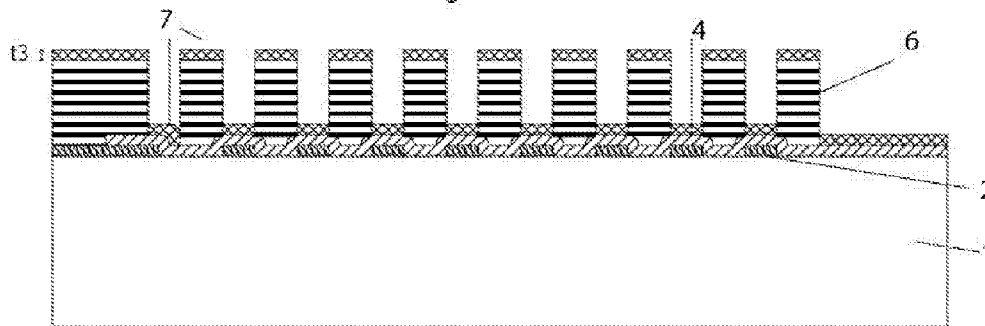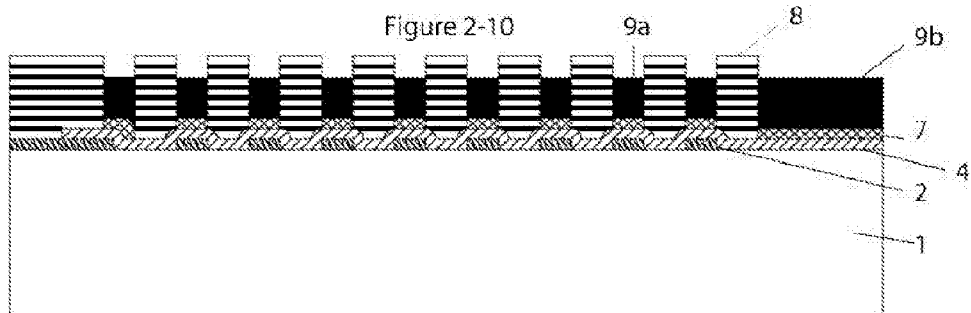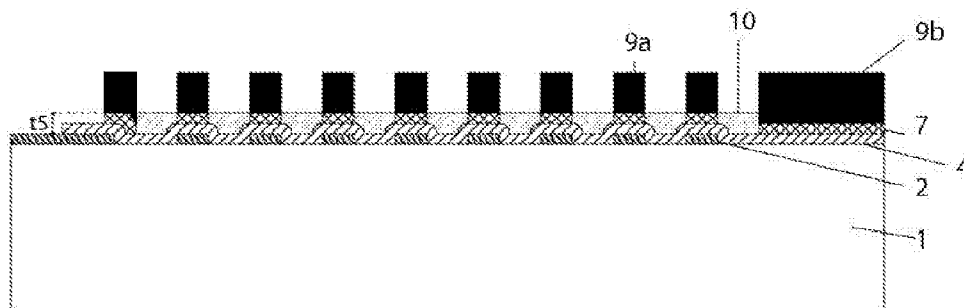
Figure 2-12

Figure 2-13
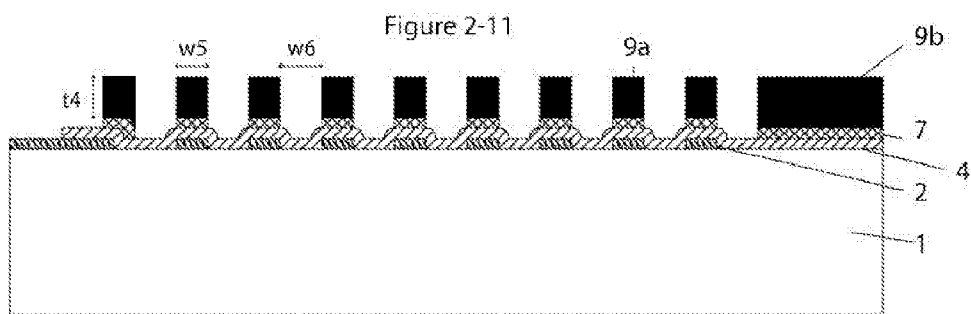
Figure 2-14

Figure 2-15

Figure 2-16
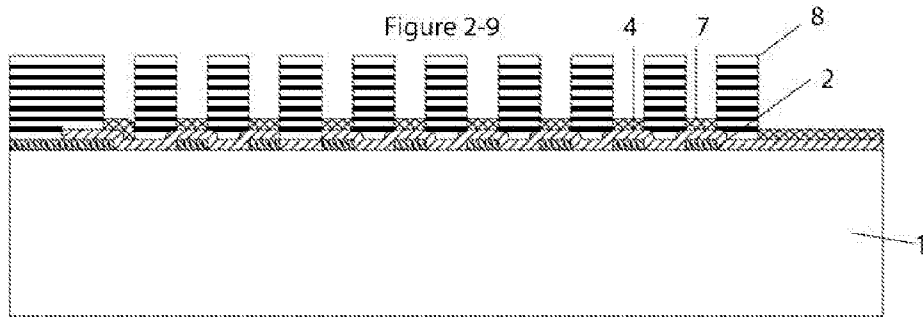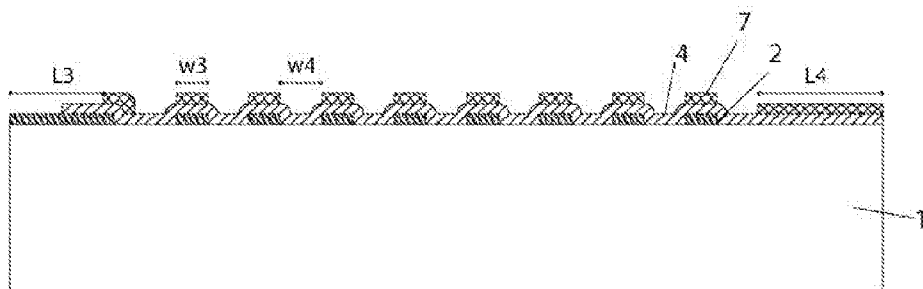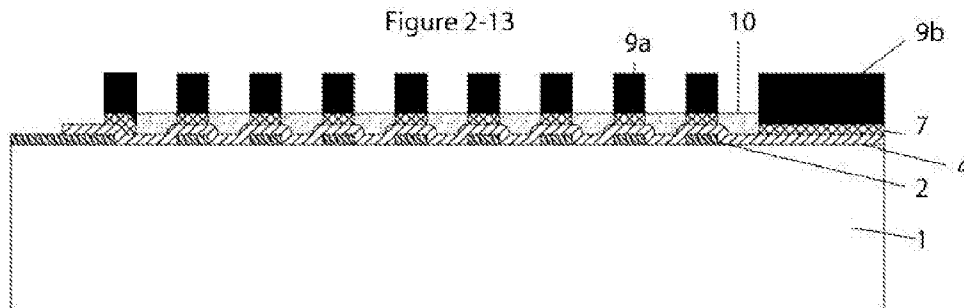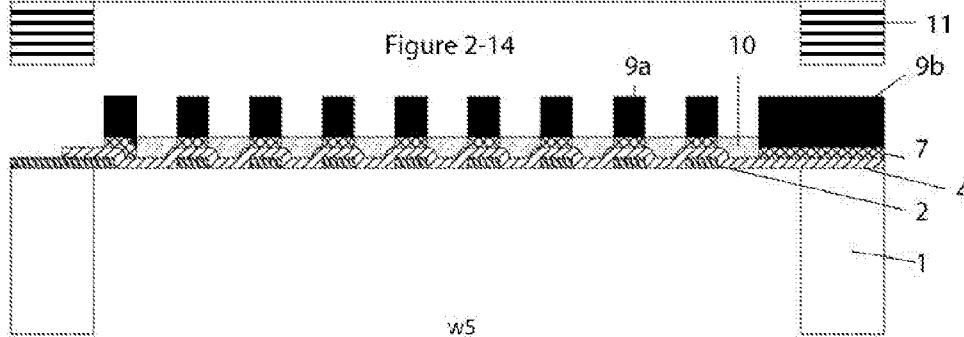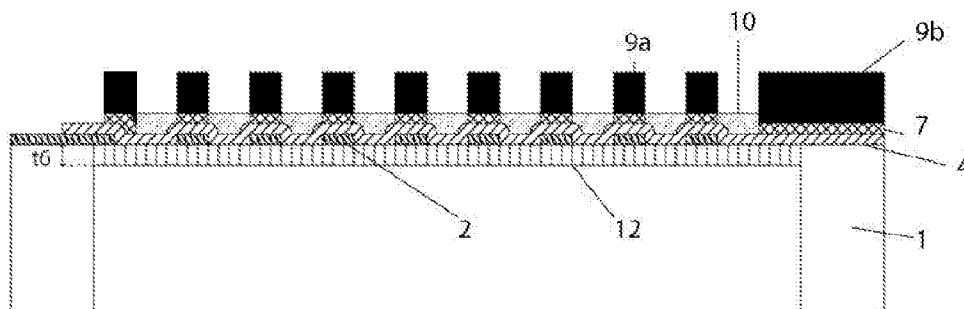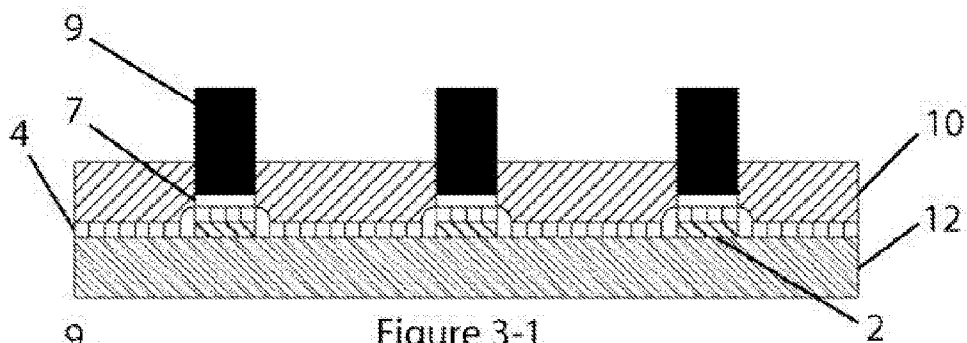
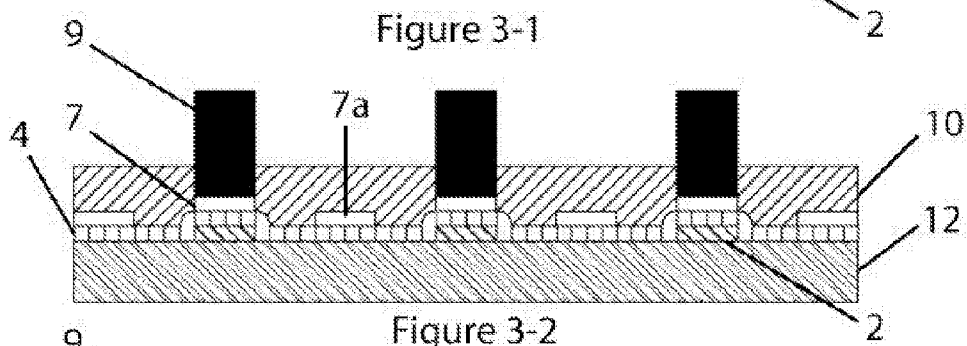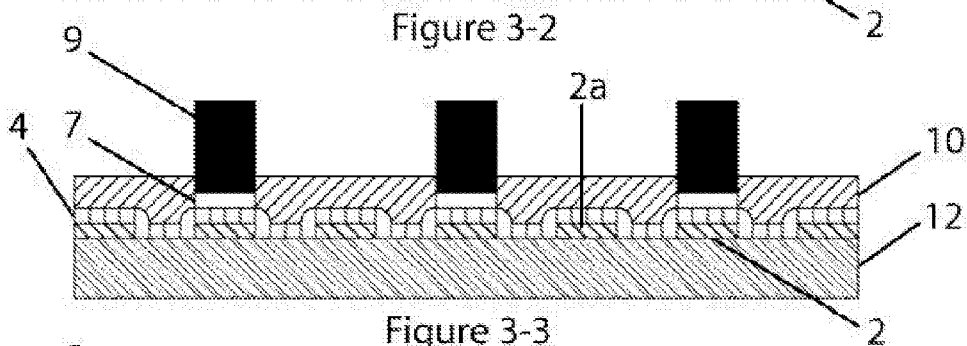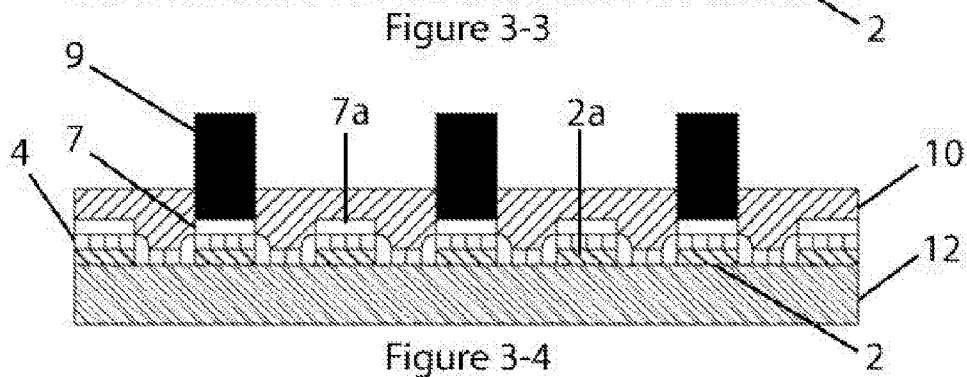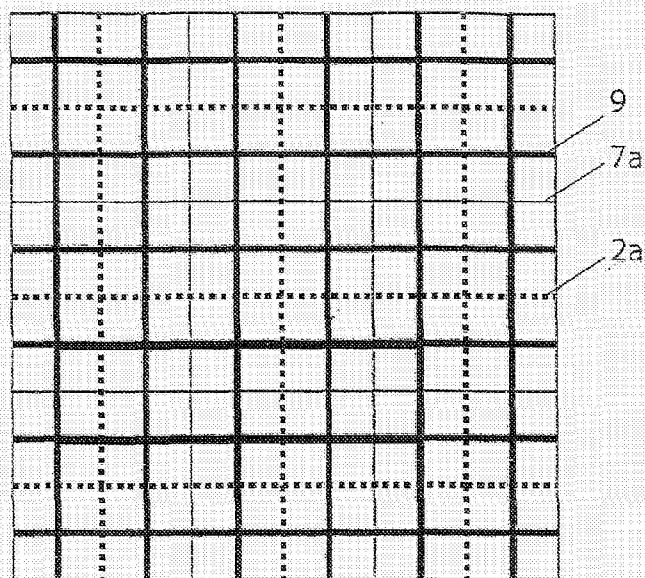Figure 3-1

Figure 3-2

Figure 3-3

Figure 3-4

9

7a

2a

Figure 4

Contact
cathode (2b)   Grid (9a)   Cathode current
collector (2)   Electrolyte (4)   Contact
anode (9b)

Reference air (13)   Heater (14)
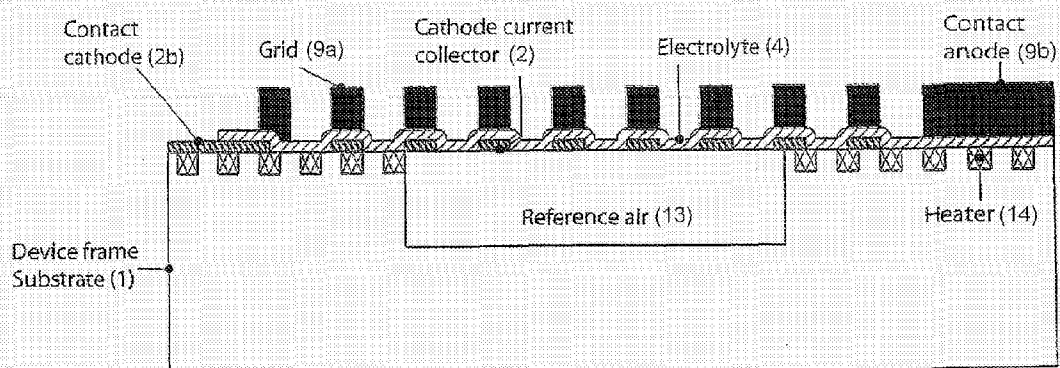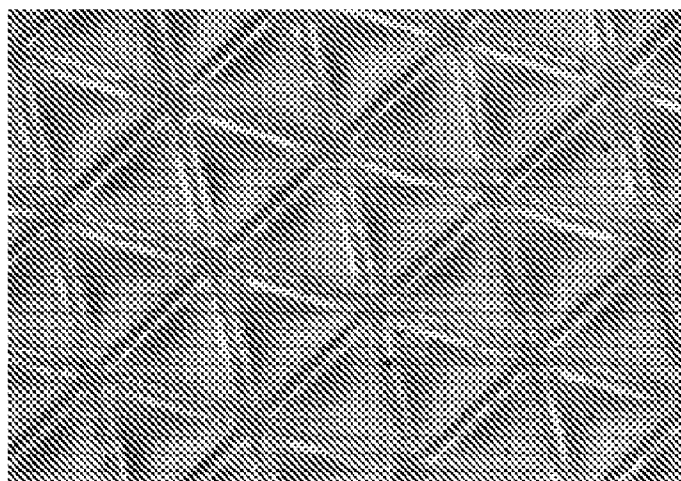
Device frame
Substrate (1)
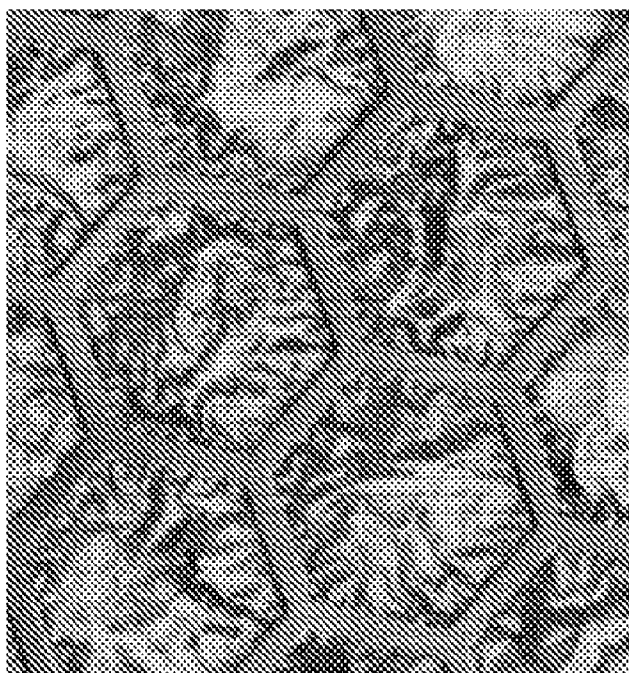
Figure 6

Fig. 5-1

Fig. 5-2

METALLIC SUPPORTING GRID FOR THIN ELECTROLYTE MEMBRANE IN SOLID OXIDE FUEL CELLS

FIELD OF INVENTION

[0001] This invention relates to miniaturized solid oxide fuel cells requiring thin electrolyte membranes including electrodes and electrode contacts.

BACKGROUND

[0002] The essential part of a solid oxide fuel cell (SOFC) consists of a ceramic plate made of an oxygen ionic conductor having the function of a solid electrolyte. The electrolyte plate is covered on the anode side by a porous metallic film, and on the cathode side by an electronic conductive oxide. Being exposed to a flow of air or oxygen (O_2), this cathode layer takes up oxygen, and supplies the necessary electrons to form oxygen ions that traverse the electrolyte plate to reach the anode. There, a hydrocarbon gas mixture is oxidized by the oxygen ions and the electron charges are given to the anode electrode. The respective electrochemical potentials on the two sides are such that a voltage difference of roughly one Volt is installed allowing for recuperation of electrical power. The operation temperature of a classical SOFC amounts to 800 to 1000° C. (see e.g. B. C. H. Steele, A. Heinzel, *Materials for fuel-cell technologies, NATURE* vol. 414, p. 345 (2001)). Operation procedures, application fields, and design depend crucially on the operation temperature. While high operation temperatures are good for large cells working continuously, high temperatures are unpractical for small cells and for automotive applications. In the first case, heat losses become too important, and in the second case, the time and energy consumption for start-up become too large. It is conceivable to operate SOFC's at temperatures as low as 500° C. (R. Doshi, V. L. Richards, J. D. Carter, X. Wang, and M. Krumpelt, *Development of SOFCs that operate at* 500° C., J. El. Chem. Soc. vol. 146, p. 1273 (1999)). Such low temperatures are compatible with concepts of small SOFC cells in the centimeter dimension, able to be employed as energy source for portable electronic and electric devices. In such markets, miniaturized SOFC's are expected to have a large potential. Micro-SOFC's would be fuelled by liquid butane for instance.

[0003] In miniaturized cells of lower temperature, the electrolyte plate or layer thickness must be reduced to reduce resistive losses inside the electrolyte. The ionic conductivity a follows an exponential law of the form:

$$\sigma = \frac{A}{T}\exp(-E_a/kT) \qquad (1)$$

where A is a constant, E_a the activation energy, k the Boltzmann constant and T the absolute temperature. The internal resistance per unit area R_i of the cell can be written as:

$$R_i = \frac{t_{el}}{\sigma} = \frac{t_{el}T}{A}\exp(E_a/kT) \qquad (2)$$

[0004] R_i is typically chosen as 0.1-0.2 Ωcm^2 to allow for currents of 100 mA/cm^2 without loss of output voltage. Taking as an example a $Ce_{0.8}Gd_{0.2}O_3$ membrane, whose activa-

tion energy amounts to 0.7 eV, the thickness must be reduced by a factor 21 when decreasing the temperature from 1273K to 823K, provided that the conductivity of the material is the same for both thicknesses. This means that the electrolyte membrane cannot be anymore a self supported one of several 100 µm to 1 mm thickness, but must be thinned down to 5-50 µm and supported by another structure. Such supporting structure described in the literature is a 300 to 1200 µm thick porous anode, consisting usually of a composite structure of nickel and yttrium stabilized zirconia (YSZ) (see, e.g. P. Holtapples, U. Vogt, and T. Graule, *Ceramic materials for advanced solid oxide fuel cells.*, Adv. Eng. Mat. vol 292, p. 292 (2005)).

[0005] An article *Thin-film heterostructure solid oxide fuel cells* by X Chen, N. J: Wu, L. Smith and A. Ignatiev, Applied Physics letters Vol. 84, Number 14, pages 2700-2702 describes a micro thin-film solid oxide fuel cell having a nickel foil substrate processed into a porous flat anode that has an array of circular pores.

[0006] In US patent application US 2005/0115889-A1 (pub. date Jun. 2, 2005) entitled "Stressed thin film membrane islands", a stiffening structure is proposed to increase the stability of thin film membranes that are closing a large opening in a substrate. The proposed solutions include a grid structure superimposed to the thin film membrane to stiffen and support the membrane. The solution proposed is based on silicon micromachining techniques including deep silicon etching to define trenches. These are filled with nitride and oxide materials by means of thermal or plasma enhanced chemical vapor deposition. There are three major problems related to that invention:

[0007] 1) The membrane needs to be perforated to grow the supporting structure, risking leakage in case of SOFC application.

[0008] 2) The supporting structure traverses the membrane, requiring insulating material for the supporting structure.

[0009] 3) The supporting structure is produced in a rather complicated, delicate and costly way.

[0010] The invention aims to remove some of these problems, and add additional functionality.

SUMMARY OF THE INVENTION

[0011] In this invention, a different way is pursued. The membrane thinness is chosen to allow for compatibility with thin film and micromachining technology. An electrolyte membrane in the thickness range of 50 nm to 10 µm—deposited for example by sputtering or sol-gel techniques—closes a 100 µm to 100 mm wide opening of a substrate of typically 0.5-1 mm thickness. A metallic grid structure with a mesh size that is usually 10 to 1000 times smaller than the substrate opening supports the membrane to avoid cracking caused by excessive stresses and buckling. In addition, the metallic grid serves as current collector, preferentially on the anode side.

[0012] This invention relates to miniaturized solid oxide fuel cells requiring thin electrolyte membranes including electrodes and electrode contacts. The thinness of the electrolyte membrane requires a supporting structure.

[0013] The invention thus provides a solid oxide fuel cell structure obtainable by selective electrochemical processing, the structure comprising:

[0014] an electrolyte membrane formed by a thin film more than 50 nm but less than 10 µm thick, covering a supporting structure made of a bulk substrate, the sup-

porting structure having at least one opening that is 100 µm to 100 mm wide and that is covered by the electrolyte membrane; and

[0015] a metallic grid applied over the electrolyte membrane and serving at the same time as structural element to support the membrane and as current collector, the metallic grid having gridlines that are higher than the membrane thickness and whose height to width ratio is larger than 0.5, preferably larger than 1 and even more preferably larger than 2.

[0016] The metallic grid usually has a mesh size about 10 to 1000 times smaller than the width of said opening.

[0017] By virtue of the grid's morphology and its aspect ratio, more space is left for the porous anode material which is easier to access. The new metallic grid is relatively thick and open, allowing better opportunities for 3-phase contact leading to better performance. It is also adapted to the expected thermal strains and stresses.

[0018] Preferably, the metallic grid is applied on top of a patterned metallic sub-layer structure, the sub-layer structure comprising a wider pattern corresponding to the applied metallic grid, and a finer pattern that is not covered by the applied metallic grid, this finer pattern being arranged for supplying a fine distribution of current and increasing the density of electrolyte-electrode boundaries exposed to the fluid, and the metallic grid is on an anode side which in use is exposed to hydrocarbon fluid.

[0019] Usually, the metallic grid is an anode current collector, and a cathode current collector structure is added on an opposite cathode side. The cathode current collector structure can have the same size and shape as the anode current collector grid, or the cathode current collector structure can have a different shape and/or be displaced with respect to the anode current collector grid.

[0020] The invention removes some of the aforesaid problems with US 2005/0115889-A1, and adds additional functionality to the supporting structure:

[0021] 1) The membrane (electrolyte in our case) is not perforated during fabrication of the supporting structure.

[0022] 2) The supporting structure is on one side only (anode) and can be made with a metallic material and with high aspect ratio.

[0023] 3) The fabrication is less complicated and less expensive, as it uses electrochemical deposition of typically nickel. The mould for the creation of high aspect ratio grid structures is the not the silicon substrate on which the membrane is grown (as in US 2005/0115889), instead we can use a patterned thick photoresist on top of the membrane to form the mold.

[0024] 4) The metal grid is used at the same time to work as current collector, thus supporting the functionality of thin porous electrodes, as typically used on the anode side.

[0025] 5) A further extension introduces a thin metallic network structure on the side opposed to the supporting metallic grid to collect the current on this side and connect to a contact pad on the same side as the other one. The side with the contacts is preferentially the anode side, thus in reducing atmosphere, in order to avoid oxidation of contact metals.

[0026] A critical issue is the stability of membranes at the operation temperature (500-600° C.). Typically-used electrolyte materials such as $CeGdO_2$ (CGO) or YSZ exhibit a large

thermal expansion of around 12 ppm/K, which in addition may depend on the oxygen partial pressure. The thermal expansion of Ni comes quite close (13 ppm/K). Hence the Ni grid and the electrolyte membrane expand by about the same amount when the temperature is raised. The substrate usually has much less expansion (Silicon: 3 ppm/K, silicon glasses: 1 to 8 ppm/K). Having a larger thermal expansion than the substrate, the membrane will buckle. The critical buckling strain

$$\varepsilon_{crit} = \frac{\pi^2 t^2}{3L^2}$$

(S. P. Timoshenko, and J. M. Gere: Theory of elastic stability, McGraw-Hill, N.Y. 1961, pp 49) for a 1 µm membrane closing a 10 mm diameter opening amounts to less than 1 ppm. A temperature change of 500° C.—as occurs when installing between room temperature and operation temperature—results in a thermal strain ($\epsilon_{op} = (\alpha_{mem} - \alpha_{sub}) \cdot \Delta T$) of up to 0.5%, thus by far larger than the critical strain. The role of the metallic grid is to partition the membrane into smaller areas exhibiting larger critical strains (for instance, a 1 µm membrane within a 100 µm wide opening of the grid exhibits a critical strain of already 0.3%). The Ni grid takes up the forces from the border of the large opening in the substrate. The grid being thicker than the membrane (usually more than twice as thick) the buckling—if occurring—is smoother and more regular than that of the thin electrolyte membrane (see FIG. 5-1 as an example) and the amplitude is lower. In addition, a metal grid is much tougher than a ceramic membrane. For large openings, a warping cannot be avoided, even with a grid of high aspect ratio. In this case a judicious design of grid will allow for a controlled warping.

[0027] The grid geometry can be adapted to expected strains. Typically the supporting grid exhibits 5 µm wide and 10 µm high grid lines (i.e. with the aspect ratio, height to width, of 2) and defining 20 to 200 µm wide grid openings (mesh size). A high aspect ratio ensures keeping a large efficiency of the cell, which is proportional to the active area exposed to the fuel gas flow divided by total area (can be called "filling factor"). Membrane thickness and diameter of grid openings can be matched to obtain locally flat membranes within the grid openings, and relax thermal stresses to form a global deformation of the grid/membrane structure. Engineering to obtain predefined buckling may yield the requirement that the optimal grid geometry at the border of the membrane might be different from that in the center of the membrane. This is anyhow true for designs inspired by spin webs. In case of a hexagonal grid, the border elements could be filled with triangles to reinforce stiffness at the border (as in FIG. 5-1).

[0028] The metallic grid plays at the same time the role of current collector. Being at the anode side, a porous Ni-electrolyte composite is deposited on top of the membrane on the grid side. The metallic grid guarantees the global connectivity of the porous layer, and allows reduction of the electrical conductivity of the porous electrode material. Preferential material for the grid is material that is well grown by electrochemical deposition, and in addition compatible with the anode-side function, such as nickel, palladium, copper, molybdenum, cobalt, ruthenium, iridium. Suitable seed layer materials are: Pt, Ir, Ru, etc., possibly also nickel or copper.

[0029] Furthermore, the sub-layer or seed layer used for the electro-deposition of the metallic grid can be extended to provide a fine distribution of current. Only parts of this seed layer are then covered by the resist forming the mould for electro-deposition. This fine distribution may be a regular sub-grid structure. Its mesh size may be decreased to reach a high density of fine distribution lines, thus approaching an artificial porous structure. The fine distribution lines could be as thin as a few 100 nm's. They could be organized as fractal structure carrying the current form the inside of the grid opening to the grid lines, having in the center a higher density of very narrow lines, and towards the grid line, a lower density of wider lines.

[0030] The metallic grid may exhibit a polygonal pattern including in particular regular polygons such as triangles, squares, hexagons and octagons or irregular shapes including spider web type shapes and fractal structures.

[0031] The invention also concerns an array of structures as described, which are fabricated on a common substrate and connected electrically to form an array of solid oxide fuel cells.

[0032] The SOFC structures of the invention are useful for current-generating applications as well as applications where they are used to generate a potential difference, e.g. when the structure is used as a gas sensor, exposed to gas in small concentrations at, say, 400-500° C.

BRIEF DESCRIPTION OF THE DRAWINGS

[0033] The invention will be further described by way of example with reference to the accompanying drawings, in which:

[0034] FIG. 1-1 shows an embodiment of a fuel cell structure according to the invention, without a cathode collector grid;

[0035] FIG. 1-2 shows another embodiment of a fuel cell structure according to the invention with a cathode collector grid;

[0036] FIG. 2 illustrates in FIGS. 2-1 to 2-16 the successive steps for the fabrication of the structure of FIG. 1-2;

[0037] FIG. 3 illustrates in FIGS. 3-1 to 3-4 variations where the anode grid is grown on a sub-layer or seed layer;

[0038] FIG. 4 is a schematic top view showing the pattern of the metallic anode grid, sub-layer or seed layer and current collector;

[0039] FIG. 5 shows in FIGS. 5-1 and 5-2 photographs of examples of different grid shapes; and

[0040] FIG. 6 shows a cross sectional view of a planar oxygen sensor.

DETAILED DESCRIPTION OF THE DRAWINGS

[0041] For convenience, the reference numbers used in the drawings are shown in Table 1.

TABLE 1

| | List of reference numbers. |
N°	Description
1	Substrate
2	Current collector cathode
2a	Additional grid lines of cathode
2b	Electrical contact of cathode
3	Photoresist Mask 1
4	Electrolyte

TABLE 1-continued

| | List of reference numbers. |
N°	Description
5	Photoresist Mask 2
6	Photoresist Mask 3
7	Sub- Seed-layer/current collector anode
7a	Intermediate sub- seed-layer
8	Photoresist Mask 4 mould
9	Grid/Electrical contact anode
9a	Metallic grid
9b	Electrical contact of the metallic grid
10	Porous anode
11	Photoresist Mask 5
12	Porous cathode
13	Reference air cavity
14	Heater

[0042] FIG. 1-1 is a schematic view of a PEN structure of a fuel cell composed of a porous cathode 12, a thin electrolyte film 4 and porous anode layers 10. The PEN is mounted on a substrate 1 and mechanically supported by a metallic grid 9a which is also a part of the anode current collector. Electrical connections 2b and 9b respectively for the anode and the cathode are both placed on the anode side of the device.

[0043] FIG. 1-2 also shows a PEN structure of a fuel cell like that of FIG. 1-1 but additionally with a current collector grid 2 on the cathode side.

[0044] FIG. 2 illustrates the process flow steps for the fabrication of the device shown in FIG. 1-2. Steps 1 to 3 are skipped for the device shown in FIG. 1-1. The process steps of FIGS. 2-1 to 2-16 are as follows:

[0045] FIG. 2-1: Deposition of a metallic layer 2 of thickness t1 by PVD on a substrate 1 of thickness to. Layer 2 will constitute the current collector on the cathode side and the electrical contact for the cathode.

[0046] FIG. 2-2: Deposition and structuration of a photosensible polymer layer 3 serving as first photoresist mask for the current collector 2 etch.

[0047] FIG. 2-3: Dry etching of the current collector 2 and removal of the photoresist mask 3. Layer 2 is now a mesh with line width w1 and line spacing w2. On the border of the membrane, an electrical contact 2b of dimension L1 is also structured.

[0048] FIG. 2-4: Deposition of the electrolyte layer 4 of thickness t2.

[0049] FIG. 2-5: Deposition and structuration of a photosensible polymer layer 5 serving as second photoresist mask for the electrolyte 4 etch.

[0050] FIG. 2-6: Dry etching of an opening ("via hole") of dimension L2 in the electrolyte 4 and removal of the photoresist mask 5. The "via hole" serves for making electrical contact with the cathode 2 via its contact 2b.

[0051] FIG. 2-7: Deposition and structuration of a photosensible polymer layer 6 serving as third photoresist mask for the lift-off of the seed layer 7.

[0052] FIG. 2-8: Deposition of a metallic layer 7 of thickness t3 by PVD over the photoresist mask 6. Layer 7 serves as seed layer for the electrodeposition and as current collector for the anode, depending on the design shown in FIG. 3.

[0053] FIG. 2-9: Removal of the photoresist 6. Seed layer 7 is structured by lift-off with line width w3 and line spacing w4. A gap of dimension L3 is not covered by layer 7. This gap serves as via for the electrical connection of the cathode 2. On

4

one border, the membrane **4** is covered by layer **7** over a dimension L**4**. The seed layer **7** is connected to an electrical contact on the border of the substrate for electrodeposition.

[0054] FIG. **2-10**: Deposition and structuration of a photo-sensible polymer layer **8** serving as mould for the electrode-posited layer **9** (9*a* and 9*b*).

[0055] FIG. **2-11**: Electrodeposition of the metallic grid **9***a* and contact **9***b* of thickness t**4**. The grid **9***a* has a line width w**5** and a line spacing w**6** (FIG. **2-12**). The metallic grid **9** also serves as electrical contact **9***b* for the anode covering a length L**4** of the seed layer **7**.

[0056] FIG. **2-12**: Removal of the photoresist mould **8**. The thickness of the metallic grid is t**4**, the line width w**5** and the space between lines w**6**.

[0057] FIG. **2-13**: Deposition of the porous anode layer **10** of thickness t**5** with a hard mask protecting the electrical contact of the cathode.

[0058] FIG. **2-14**: Deposition and structuration of a photo sensible polymer layer **11** serving as fifth photoresist mask for the substrate **1** backside etch.

[0059] FIG. **2-15**: Dry etching of an opening of size w**5** in the substrate **1**.

[0060] FIG. **2-16**: Deposition of a porous cathode layer **12** of thickness t**6** on the backside of the substrate **1**.

[0061] FIG. **3-1** is a schematic cross-sectional view of a part of the metallic grid **9** supporting the electrolyte **4**, anode **10** and cathode **12**. In this example, the whole sub- or seed-layer **7** is covered by the metallic grid **9**. The current collector of the cathode **2** is placed under and only under each grid element.

[0062] FIG. **3-2** is like FIG. **3-1** where in addition some parts **7***a* of the sub- or seed-layer **7** are not covered by the metallic grid **9** and serve as current collector for the anode **10**.

[0063] FIG. **3-3** is like FIG. **3-1**, where a current collector of the cathode **2** is introduced that has its lines at the same position as the lines of the grid **9***a* and additional grid lines **2***a* in-between.

[0064] FIG. **3-4** represents a combination of FIGS. **3-2** and **3-3**. Parts **7***a* of the seed layer **7** are not covered by the metallic grid **9** and serve as current collector for the anode **10**, and some parts **2***a* of the current collector of the cathode **2** are not at the same position as the metallic grid **9**. In this case, the extra lines **7***a* of the seed layer **7** and **2***a* of the cathode **2** can overlay one another (as shown) or can intersect with one another.

[0065] FIG. **4** is a schematic top view of the metallic grid **9**, seed layer **7** and current collector of the cathode **2**, showing the extra seed-layer lines **7***a* and the extra cathode collector lines **2***a*. The line widths of the three networks are between 0 μm and 50 μm and not necessarily equal. The spaces between the lines of these three networks are between 1 μm and 500 μm and not necessarily equal. The centres of the cells of the different networks can be super-imposed or displaced by distances between 1 μm and 100 μm.

[0066] FIG. **5-1** is a photograph of an example of a nickel grid of triangular shape on top of a free-standing CGO membrane. Side length of triangles: 50 μm. In this case, the triangular shapes are arranged to form a series of hexagons.

[0067] FIG. **5-2** is a photograph of an example of a nickel grid of hexagonal shape on top of a free-standing CGO membrane. Side length of hexagons: 50 μm. In this photo, the controlled buckling of the membrane in the grid is clearly visible.

[0068] The invention is a Positive electrode-Electrolyte-Negative electrode (PEN) structure of a solid oxide fuel cell including an anode grid **9** supporting an electrolyte membrane **4**. The invention is used for mid-temperature to medium temperature range solid oxide fuel cells (300° C.-600° C.). The originality of the invention is the grid **9** serving as mechanical support of the thin electrolyte layer **4**, as part of anode and as link for the electrical connections. This design allows placing the two electrical contacts (anode and cathode) on the same side of the support and facilitates the current collection. The supporting grid prevents thermal cracks in the electrolyte membrane **4** and allows improving the reactive area of the cell. The anode and cathode triple phase boundary lines (TPL) can also be improved by the inclusion of micro structured current collector meshes on the both sides of the electrolyte. The original and easy micro fabrication process of this structure is also part of the present invention.

[0069] The invention is related to a PEN structure for fuel cell applications comprising:

[0070] a substrate **1** with a "large" opening of width w**5** from 100 μm to 100 mm;

[0071] an electrolyte membrane **4** closing the said opening;

[0072] a metallic grid **9** supporting the membrane **4** and being part of the anode;

[0073] an anode **10**;

[0074] a cathode **12**;

[0075] a current collector mesh formed by the grid **9** on the anode side;

[0076] a current collector mesh **2** on the cathode side;

[0077] an electrical contact **9***b* to the anode, located on the anode side; and

[0078] an electrical contact **2***b* to the cathode, also located on the anode side.

[0079] The substrate **1** is a silicon, glass, Foturan™, Pyrex™ or quartz flat wafer with diameter of for example 10 mm to 300 mm (FIG. **2-1**).

[0080] In a first design, the electrolyte **4** is directly deposited onto the substrate **1** (possibly using a buffer layer) (FIG. **1-1**). In a second design, a metal mesh for cathode current collector **2** is deposited and patterned first (FIG. **1.1**, FIG. **2-1**, **2-2**, **2-3**). It is deposited by PVD, CVD, evaporation or PLD (pulsed laser deposition) and structured using photolithography and dry or wet etch. The collector **2** has the form of a two-dimensional mesh. The collector material is a conductive metal or oxide. The thickness t**1** of the collector **2** is between 50 nm and 200 nm, its line width between 1 mm and 10 μm and the spaces between lines between 5 μm and 500 μm.

[0081] The electrolyte **4** is deposited by thin film technology (magnetron sputtering, pulsed laser deposition, chemical vapour deposition, spray pyrolysis, sol gel method, evaporation, screen printing, tape casting) and has a thickness between 50 nm and 10 μm (FIG. **2-4**). The electrolyte **4** is an oxygen ion conductor, typically $ZrO_2{:}Y_2O_3$ (YSZ) or $Ce_xGd_{1-x}O_{2-y}$ (CGO), or other doped or undoped oxide ion conductors that usually exhibit the crystal structure of fluo-rites (for example: ZrO_2, CeO_2), corundum (for example: Y_2O_3), perovskite (for example: $La_{1-x}Sr_xGa_{1-y}Mg_yO_3$), tungsten bronzes (for example: $SrBaNbO_6$), pyrochlores or Aurivilius phases (for example: $Bi_4Ti_3O_{12}$). The electrolyte film is removed at the border where the contact to the cathode **2***b* is foreseen (FIGS. **2-5** and **2-6**, dimension L**2**).

[0082] The electrolyte membrane **4** is supported by grid **9** (FIGS. **2-10** to **2-12**). For its fabrication, a photoresist **6** is

deposited and patterned first (FIG. 2-7) to allow for deposition of a seed layer 7, which is patterned by dissolving the resist (lift-off technique) arriving at the schematic structure of FIG. 2-9. The seed layer 7 is an electrical conductive metal such Cr, Au, Al, Cu, Pt, Pd, Ni, Mo, Ag, Ce, Gd or combination thereof. It is deposited preferentially by means of evaporation or magnetron sputtering. In the next step the mould 8 is prepared in the form of a patterned resist. The grid structure 9 is grown inside the mould by electrochemical deposition, the current being supplied through the seed layer 7 (FIG. 2-11), which is connected on the wafer level to a power supply. Alternatively, the deposition can be performed by electroless plating. The growth of layer 9 yields the grid structure 9a, the anode contact 9b, which is of the same body as the grid. The material of the grid 9 is selected among electronically conductive metals (including Ni, Cu, Fe, Pt). The height t4 of the grid 9 is usually at minimum twice as thick as the electrolyte membrane 4 and between 1 μm and 100 μm, its line width w5 between 1 μm and 100 μm. The openings in the grid have dimensions w6 between 5 μm and 500 μm.

[0083] The grid 9 mechanically supports the electrolyte membrane 4 and serves as current collector for the anode layer 10. The grid 9 covers the central part of the substrate to reach contacts for external electrical connections via contact 9b. The anode layer 10 is deposited by PVD, spray pyrolysis, CVD, PLD or evaporation over and in the spaces of the grid 9, covering the free surface of the electrolyte 4 (FIG. 2-13). The cathode contact on width L3 is protected by a sacrificial layer to avoid a short (by dry or wet etching or by lift-off). The thickness t5 of the anode layer 10 is between 50 nm and 5 m. The material of the anode 10 is a porous composite of an electronic conductor (Ni, Pt, Ce, Gd . . .) and an ionic conductor (YSZ, CGO, . . .), or a porous mixed conductor (LSCF, LSC . . .).

[0084] The liberation of the membrane 4 is preferentially carried out by deep dry etching process as available for silicon and silicon glass. First a thick resist 11 is deposited, and patterned by photolithography (FIG. 2-14). The resist serves as mask for deep dry etching. An opening is formed into the substrate 1, of width w5 (FIG. 2-15), measuring 100 μm to 100 mm.

[0085] The cathode layer 12 is deposited by PVD, spray pyrolysis, CVD, PLD or evaporation over the electrolyte on the opposite side of the anode through the large opening in the substrate (dimension w5) of the support (FIG. 2-16). Cathode layer 12 covers the cathode current collector 2, to which there is automatically an electrical contact. The thickness t6 of the cathode is between 50 nm and 5 mm. The material of the cathode is a porous composite of an electronic conductive oxide (IrO_2, RuO_2) and an ionic conductor (YSZ, CGO, LSC, LSCF . . .) or a porous mixed conductor such as (LaSr)(CoFe) O_3 (LSCF) or $La_{1-x}Sr_xCoO_3$ (LSCO)

[0086] Variations of the design shown in FIGS. 3-1 to 3-4 relate to the use of a seed layer 7 as current collector mesh on the anode side, and of a thin film structure as current collector on the cathode side. In FIG. 3-1, the grid structure 9 is grown on the entire seed layer 7. On both sides, no fine distribution of current is foreseen. In FIG. 3-2, a part of the seed layer 7 is used to distribute on a smaller scale the current within each opening of the grid 9. This fine distribution can be effectuated by a multitude of electrically connected lines 7a. The simplest case, with one additional sub-lattice is shown (as in FIG. 4). In FIG. 3-3, an additional thin current collector 2 is introduced on the cathode side, one cathode mesh having the same pat-

tern as and being below the structure 9 of the anode side, and the additional cathode grid 2a being spaced in between the anode grid 9. As a further variation, the two current collectors might be shifted with respect to each other (FIG. 4).

[0087] Use as Gas Sensor

[0088] In addition to the generation of electricity, the structure according to the invention can also be used as a gas sensor wherein the structure is exposed to gas and used to generate a voltage as a function of a gas pressure. Theoretically, the output voltage ΔV of a solid electrolyte stack is given by the expression:

$$\Delta V = -\frac{RT}{ZF} \ln\left(\frac{p_{O_2}(1)}{p_{O_2}(2)}\right) \tag{3}$$

$$= 0.022 \cdot T\left[\frac{mV}{K}\right] \ln\left(\frac{p_{O_2}(1)}{p_{O_2}(2)}\right)$$

where $p_{O2}(1)$ and $p_{O2}(2)$ are the partial oxygen pressures on the two sides, R and F are the gas constant and Faraday constant, respectively. Z is the total charge per gas molecule, i.e. 4 for oxygen ($2xO^{2-}$). Sensors using this principle are in use for tuning the fuel-to-air ratio of engines (Lambda sensors). They are made of bulk YSZ (Yttria stabilized zirconia). A recent published version with planar geometry, still using bulk or thick film YSZ, is shown in E. I. Tiffee, et al, Electrochim. Acta 47 (2001) 807. A lower thermal capacity and a built-in heater serves to shorten time between start of the engine and reaching operation temperature of the sensor, as compared to the first generation k-sensors.

[0089] It is clear that a thin film version of this device according to this invention would exhibit even smaller thermal capacities, and need less power to heat the sensor. It could also be used at lower temperatures.

[0090] Such a thin film gas sensor according to the invention is shown in FIG. 6. This gas sensor has one electrolyte layer 4 sandwiched between the anode grid 9a and cathode 2. The substrate 1 is micromachined to provide a cavity 13 adjacent the cathode side to contain the reference air or other gas. The pO2 is measured by the voltage between the anode grid 9a and the cathode 2. A heater 4 is formed as part of the substrate and can consist of metal wires heated by the Joule effect (see *Local growth of sol-gel films by means of micro-hotplates*, Calame F. Barborowski J., Ledermann N., Muralt P., Gentil S. and Setter N., Integrated Microelectrics 54: 549-556 2003.

[0091] One can either measure the open circuit voltage, or the limiting current in the amperometric mode, at which oxygen ions are pumped through the ion conductor until a limit is reached depending on the supply of oxygen or reducing gas (controlled by diffusion barrier) or ions (controlled by catalytic processes at electrodes). Descriptions of operation modes and electrolyte behavior in YSZ are for instance found in R. Ramamoorthy, P. K. Dutta, S. A. Akbar, J. Mat. Science 38 (2003) 4271; and B. Y. Liaw, W. Weppner, J. Electrochem. Soc. 138 (1991) 2478.

[0092] For an estimation of the sensitivity we consider potentiometric measurements. In a sensor with a dilute reducing gas, we would have a small pressure difference. We write the pressures as:

$$p_{O2}(2)=p_{ref}; p_{O2}(1)=p_{ref}+\Delta p.$$

[0093] As we can linearise the logarithm around one as $\ln(1+x)=x$, we should measure at 800 K a voltage of:

$$\Delta V = 17.2[mV]\frac{\Delta p}{p_{ref}} \qquad (4)$$

[0094] This value has to be appreciated in relation to the intrinsic noise of the cell, and to the characteristics of the electronics. The signal to noise ratio of the sensor is the crucial quantity to be evaluated. The noise source can be assumed to be the internal resistance of the element given by the ionic conduction resistivity. So we would deal with a Johnson noise, or resistor noise described by:

$$V_n = \sqrt{4kTR\Delta f} \qquad (5)$$

[0095] Today CGO membranes can be produced with a conductivity of 100 S/cm at 500° C. An element with 100 μm square and 1 μm thickness thus has a resistance R of $0.01*_{10}{}^{-4}/10^{-8}=100$ Ohm. At 800 K, and a bandwidth of 10 Hz one obtains a noise voltage of 7 nV.

[0096] The ratio of noise equivalent pressure difference and reference pressure is calculated as:

$$\frac{\Delta p_n}{p_{ref}} = \frac{7 \text{ nV}}{17.2 \text{ mV}} = 4\cdot 10^{-7}$$

[0097] Hence, the sensor has the potential to reach a ppm resolution. No literature on noise evaluation of solid oxide electrolyte sensors was found. However, for H_2S sensors working by means of a polymer proton conducting membrane noise limits of less than 100 ppb are reported in G. Schiavon et al, Anal. Chem. 67 (1995) 318. There is one article on noise evaluation of oxygen conductors [C. M. Van Vilet, J. J. Brophy, Phys. Rev. B 47 (1993)11149].

[0098] The simple picture of equation 5 is probably not quite correct. At low frequencies, the noise is not white (independent of frequency). Instead, it was found that the noise increases with lowering frequency like $f^{-3/2}$. For this reason, the measurement should be preferentially done in a modulation mode at a frequency above 10 Hz in order to reduce the noise. The most natural way is to modulate the temperature. A low thermal capacity and a fully integrated heater are prerequisites to achieve low thermal time constants, and efficient heating. Both arguments speak in favour of thin film MEMS structures according to this invention.

[0099] Equation 3 is strongly modified by the role of the electrodes. The electrolyte material is not directly exposed to the gases. The effective oxygen partial pressure is a function of catalytic reactions at the electrodes, and of the ion exchange at the electrode interfaces, or more explicitly a the triple line boundaries between gas, electrolyte and electrode. In the article L. P. Martin, R. S. Glass, J. Electrochem. Soc. 152 (2005), a bulk YSZ hydrogen sensor was investigated yielding 300 mV at 1% hydrogen. Both sides were exposed to the same gas. The voltage difference in this case was due to the different effect of Pt electrodes on the one side, and ITO (indium tin oxide) electrodes on the other one. At the Pt side oxygen reduction is predominant, while at the ITO side, hydrogen oxidation. Such phenomena may also allow for a new type of design, where the electrodes are both on the same side, and the membrane structure would only serve to reduce the heat capacity.

[0100] For the gas sensor application, the same materials apply as for the above-described SOFC structure. The nickel grid can however be made thinner due to the greatly reduced current. Making the structure with small heat capacity is advantageous to modulate temperature for better signal to noise ratios compared to the bulk version. Advantageously, for the gas sensor application the structure will be combined with an on-chip heating system in view of the fact that at the low gas pressures used there is insufficient gas consumption to generate the necessary heat at the operating temperature.

1. Solid oxide fuel cell structure obtainable by selective electrochemical processing, the structure comprising:
   an electrolyte membrane formed by a thin film more than 50 nm but less than 10 μm thick, covering a supporting structure made of a bulk substrate, the supporting structure having at least one opening that is 100 μm to 100 mm wide and that is covered by the electrolyte membrane; and
   a metallic grid applied over the electrolyte membrane and serving at the same time as structural element to support the membrane and as current collector, the metallic grid having gridlines that are higher than the membrane thickness and whose height to width ratio is larger than 0.5.

2. Structure of claim 1, wherein the metallic grid has a mesh size about 10 to 1000 times smaller than the width of said opening.

3. Structure of claim 1, wherein:
   the metallic grid is applied on top of a patterned metallic sub-layer structure,
   the sub-layer structure comprises a wider pattern corresponding to the applied metallic grid, and a finer pattern that is not covered by the applied metallic grid, said finer pattern being arranged for supplying a fine distribution of current and increasing the density of electrolyte-electrode boundaries exposed to the fluid, and
   the metallic grid is on an anode side which in use is exposed to hydrocarbon fluid.

4. Structure of claim 1, wherein the metallic grid is an anode current collector, and a current collector structure is added on an opposite cathode side.

5. Structure of claim 4, wherein the cathode current collector structure has the same size and shape as the anode current collector grid.

6. Structure of claim 4, wherein the cathode current collector structure has a different shape and/or is displaced with respect to the anode current collector grid.

7. Structure of claim 4, comprising a first electrical contact to the metallic anode grid, the first contact being located on an anode side of the structure, and a second electrical contact to the cathode, the second contact also being located on the anode side of the structure

8. Structure of claim 1, wherein the electrolyte thin film is selected from CeO_2:Gd_2O_3 (CGO), ZrO_2:Y_2O_3 (YSZ), and doped or undoped oxide ion conductors that exhibit the crystal structure of fluorites, corundum, perovskite, tungsten bronzes, pyrochlores or Aurivilius phases.

9. Structure of claim 1, wherein the metallic grid is made from at least one metal selected from Ni, Cu, Pt, Cr, Mo, Ag, Co, and Pd.

10. Structure of claim 1, further comprising a porous anode film in particular selected from NiOx and Ni-(electrolyte) composite.

11. Structure of claim 1, further comprising a porous cathode film in particular selected from a porous mixed conductor such as (LaSr)(CoFe)O$_3$ (LSCF) or La$_{1-x}$Sr$_x$CoO$_3$ (LSCO); and composites of an electronically conductive oxide and an ionically conductive oxide.

12. Structure of claim 1, wherein the grid exhibits a polygonal pattern including in particular regular polygons such as triangles, squares, hexagons and octagons.

13. Structure of claim 1, wherein the grid exhibits irregular shapes including spider web type shapes and fractal structures.

14. An array of structures of claim 1, which are fabricated on a common substrate and connected electrically to form an array of solid oxide fuel cells.

15. A method of producing the structure claim 1 by photolithographic patterning and electrochemical, physical and chemical vapour processing of successive layers on an etchable substrate, wherein the membrane and the metallic grid are applied to the substrate, and the substrate is etched to provide said opening.

16. The method of claim 15, wherein the substrate opening is etched by dry etching in SF$_6$ gas or by wet etching in alkaline solutions.

17. The method of claim 15, wherein the metallic grid is moulded in a polymer mould, in particular of photoresist.

18. A gas sensor comprising a structure according to claim 1, wherein the structure is exposed to gas and generates a voltage as a function of gas pressure.

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